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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Processes for the preparation of Terephthalic Acid and the preparation of Linear Polyesters therefrom

We, TEIJIN LIMITED, a Japanese body corporate of No. 1, Umeda, Kita-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

THIS INVENTION relates to a process for the preparation of terephthalic acid in a form suitable for use in polyester production by direct esterification, and also to a process for the preparation of linear polyesters using this form of terephthalic acid.

It is known to prepare terephthalic acid, by heating a di- or mono-alkali salt of an aromatic carboxylic acid, such as dipotassium phthalate or potassium benzoate, in an inert gaseous atmosphere, to a temperature of about 360°-460°C. to cause thermal rearrangement into a dialkali terephthalate, and then reacting the product with a substance which forms an acid upon dissolving in water, such as a mineral acid, an organic acid, carbon dioxide gas or sulphurous anyhydride. It is also known to produce high purity terephthalic acid by converting terephthalic acid or derivatives thereof, obtained by a process other than that described above to the corresponding metal salt or ammonium salt, subjecting this salt to refining and other optional treatments, and then reacting it with a substance which forms an acid upon dissolving in water, such as a mineral acid, an organic acid, carbon dioxide gas or sulphurous anhydride. The bulk density of the terephthalic acid obtained by these processes is of the order of 0.3-0.6, depending on the production conditions employed.

It is also known to prepare on an industrial scale linear polyesters, in which the main acid component is terephthalic acid, and which can be formed into shaped articles such as fibres or film, by the condensation polymerization of a bis-(hydroxyalkyl)-terephthalate, or a low molecular weight polymer thereof, obtained by an ester-interchange between a dialkyl terephthalate and a glycol. In such processes the terephthalic acid component is not reacted directly with a glycol, but is first converted to its dialkyl ester and then reacted with a glycol. This is because the alkyl esters can be purified more easily than terephthalic acid, and also because they are soluble in glycols and so enable a homogeneous reaction to be carried out, thereby producing polyesters of excellent colour tone and properties. Clearly, if terephthalic acid could be directly reacted with an alkylene glycol to form a bis-(hydroxyalkyl)-terephthalate or a low molecular weight polymer thereof, and then subsequently a linear polyester, the step of preparation of dialkyl terephthalate could be omitted with consequent economic advantge.

For convenience a process for producing polyesters by direct reaction of terephthalic acid, or mixtures of terephthalic acid with at least one different organic bifunctional acid, with glycol will be referred to herein as "direct esterification method"; whilst the terephthalic acid or mixture of terephthalic acid with at least one different organic bifunctional acid used in the direct esterification will be referred to as "terephthalic acid component."

Techniques for the preparation of polyesters by direct esterification have been developed because of the economical advantage of such a process. For example, the Specifications of Patents Nos. 578,079 and 777,628 disclose such techniques. However, as is well known, the direct esterification is necessarily a heterogeneous phase reaction, i.e. solid-liquid system, since terephthalic acid is not very soluble in glycol, and the reaction is carried out in a slurry. Thus, for example, when direct esterification is carried out using a mol ratio of ethylene glycol to terephthalic acid of 1:3 (as in the Specification of Patent No. 777,628) the reaction mixture thickens

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and may be a slurry of high concentration in the early stage of the reaction. Considerable power is required to stir such a slurry, and hence uniform mixing of the reaction mass becomes difficult. Consequently, not only the quality of the polymer obtained by the condensation polymerization is adversely affected and its colour tone impaired, but also it is difficult to control the polymer quality, and moreover these tendencies are increased in industrial scale reactors. If a large amount of ethylene glycol is used to lower the viscosity of the reaction mixture and to form a slurry of low concentraton, the direct esterification process is economically disadvantageous since the amount of ethylene glycol to be recovered is increased. Furthermore the greater the amount of alkylene glycol used, the more polyester is formed by etherification of the alkylene glycol, and this results in a lowering of the softening point of the desired polyester. Thus, use of a large excess of ethylene glycol (above that necessary for the direct esterification) is unsatisfactory.

It has now been found that a significant improvement is obtained in the direct esterification method if the terephthalic acid component has a bulk density of at least 0.8 and a particle size of at most 8 mm. Accordingly the present invention provides a process for the production of terephthalic acid, or a mixture of terephthalic acid with at least one different organic dibasic acid, suitable for the formation of polyesters by direct reaction with a glycol, which comprises compressing the acid or mixture of acids and thereafter optionally crushing the compressed mass, the compression, and crushing if used, being such as to give a product having a bulk density of at least 0.8 and an average particle diameter of not more than 8 mm. Also the invention includes within its scope a process for the preparation of polyesters by reacting the above-described high density terephthalic acid component with a glycol to form a bis-(hydroxyalkyl)-terephthalate or a low molecular weight polymer thereof, and then polymerising the resultant reaction product by heating under reduced pressure. Preferably the terephthalic acid component should be compressed so that its bulk density is at least 0.9.

The other bifunctional acids which may be used in admixture with terephthalic acid include adipic, sebacic, isophthalic, bibenzoic acids, and aromatic oxycarboxylic acids. These acids are generally used in an amount less than 25 mol %, based on the total acid component, in the production of fibre or film-forming polyesters.

As the glycols which may be reacted with the terephthalic acid component, there may be used aliphatic, cycloaliphatic and aromatic glycols of 2-10 carbon atoms, such as ethylene glycol, butylene glycol, neopentyl glycol, 1,4-dimethylol-cyclohexane; or glycols having an ether bond such as diethylene glycol; or 2,2-bis[4-(β-hydroxyethoxy)-phenyl]propane may be used. These glycols may be used singly or in combination.

"Bulk density" and "average particle diameter" as used herein, are determined as follows:—

Bulk Density (BD)

The sample is lightly charged into a 200 cc graduated cylinder without any compressing to about 80% of the capacity of the cylinder. After tapping the cylinder at the bottom three times with the palm of the hand, the volume of the sample (Vcc) is measured, and its weight (Wg) is determined. The bulk density (BD) is defined by the equation below.

$$BD = \frac{W}{V} \text{ (g/cc)}$$

Average Particle Diameter

"Particle diameter" (Ds) is defined as the diameter of a spheroid of volume equal to that of the particle, and is expressed by the following formula:

$$DS = \left(\frac{6}{\pi} \cdot V\right)^{1/3} \text{ (mm)}$$

wherein V being the volume of the particle (mm^3).

The average particle diameter of the sample (D_{ave}) is defined as follows:

$$D_{ave} = \left(\frac{\varepsilon Dsi^3 Ni}{\varepsilon Ni}\right)^{1/3} \text{ (mm)}$$

wherein Dsi is the diameter of a certain particle, and Ni is the number of the particles in the sample having the particle diameter (Dsi).

When the particles are very fine, calculation of the average particle diameter of the sample by the above formula is difficult, but in this case, the average particle diameter will be below 8 mm.

A convenient method for preparing the terephthalic acid component is as follows. Terephthalic acid powder is compressed either by charging in a container under an elevated pressure, or by passing between two rotating rollers. In the former case the capacity and the shape of the container may be so chosen that the compressing operation produces tablets, and by so doing, it is possible to make the average particle diameter of the compressed product not more than 8 mm. However, when the capacity of the container causes the average particle diameter of the

product to become greater than 8 mm, or when two rotating rollers are used for compression (only one of the two rollers need be positively driven) it is normally necessary to crush the compressed product to produce an average particle diameter of not more than 8 mm. The shape of the compressed terephthalic acid need not be uniform, and pieces of various shapes may be present. The compressing means, or compressing and shaping means, are not limited to that described above, but may be any suitable means or apparatus.

Thus, by compression of the terephthalic acid component, its bulk density can be readily raised to at least 0.8. The greater the compressive pressure employed, the closer the bulk density of the compressed terephthalic acid component approaches to the specific gravity of terephthalic acid, which is about 1.6-1.7. (The value varies slightly, according to the method of measurement.) The more the compressed product is crushed, the smaller becomes its average particle diameter, but if the diameter is made too small, the bulk density will become less than 0.8. In compressing the terephthalic acid component, if the material is in a moistened state the compressing effect is increased, and shaping of the component is easier. However, it is also possible to compress, or compress and shape, dry terephthalic acid component to the desired degree. It is preferred to compress and shape the terephthalic acid component to a uniform shape.

Some of the advantages of the present invention over the prior known processes will now be described.

When polyester is prepared by direct esterification using the high density terephthalic acid component of the present invention, during the first half of batch-type esterification reaction the product takes form of a slurry of high concentration, the apparent viscosity of which is much less than that of the reaction system using an acid component of lower bulk density. Thus the power required for stirring the slurry during the esterification reaction is reduced. If the terephthalic acid component of the invention is employed in continuous-type esterification, uniform stirring can be easily practised even when the acid compenent and glycol component are fed separately into the reactor, and consequently the desired reaction can be easily and continuously performed. Again when the two components are fed into the reactor in form of a slurry, transfer is easy.

The polyester produced according to the present invention has a high quality and in particular it has a uniform softening point and colour tone.

Again, when the terephthalic acid component of the invention is directly reacted with a glycol (direct esterification) to form a bis-(hydroxyalkyl)-terephthalate or its low molecular weight polymer, the rate of reaction is no less than that when a commercially available terephthalic acid is used. This is also an unexpected advantage.

In the production of polyesters by the direct esterification using the high density terephthalic acid component of the invention, there may be added, as a direct esterification catalyst compounds such as alkali metals, alkaline earth metals, lead, zinc, manganese and cobalt, either singly or in combination. Also at the time of polymerization, known catalysts such as compounds of antimony, germanium, titanium, zinc, tin and silicon may may be added, and also phosphorus compounds may be added as stabilizer. Likewise known inorganic or organic pigments and/or dyestuffs may be added for delustering and colouring.

The invention will be further described in the following Examples in which color tone is the value set forth in ASTM, D1482-57T, and an increase in +b value denotes that the yellowing of the sample is increased.

Example 1

15 kg of dipotassium terephthalate were dissolved in 110 litres of water and heated to 85°C. 6N hydrochloric acid was gradually added with stirring to the solution until the pH of the liquid phase reached 1. The resultant precipitate was filtered by a filter press, and formed into a slurry with 100 litres of hot water, heated to 80°C. The slurry was stirred for 30 minutes, filtered under pressure, and then washed with about 50 litres of hot water. By crushing the resultant cake, after drying, 10.0 kg of terephthalic acid were obtained, which had a bulk density of 0.45.

A portion of this powdery terephthalic acid (A) having a bulk density of 0.45 was made into tablets (10ϕ $\times$ 3 m/m) by compressing and shaping at room temperature by means of a rotary tabloid machine having the maximum tablet-forming pressure of 5 tons, and crushed in a gutter mill. The terephthalic acid tablets (B) thus obtained had a bulk density of 0.86, and an average particle diameter of about 0.1 mm. At the time of compressing and shaping the terephthalic acid (A), its water content was 1.0%.

The terephthalic acid (A) and (B) were each made into a slurry with ethylene glycol, and the respective apparent viscosity of each slurry was measured at room temperature with a rotary viscometer, and the results obtained were as shown below:

Vixcosity of Slurry (poise)

E.G./Terephthalic Acid (mol)	Terephthalic Acid (A)	Terephthalic Acid (B)
1.6	300	68
2.0	280	48
3.0	120	14
4.0	25	2.4
6.0	6.9	1.5

EXAMPLE 2

70 kg of monopotassium terephthalate were made into a slurry with 320 litres of water, heated to 90°C., and 54.9 kg of phthalic anhydride were gradually added to the slurry with stirring. After stirring for an additional hour, the reaction product was filtered while it was hot by means of a centrifugal filtering machine, and was simultaneously washed with about 20 litres of hot water. The cake thus obtained was made into a slurry with 300 litres of hot water, heated to 80°C. with stirring for 30 minutes, filtered through a centrifugal filtering machine, and simultaneously washed with about 20 litres of hot water. When the resultant cake was dried and crushed, 53 kg of terephthalic acid having a bulk density of 0.52 were obtained. This terephthalic acid was compressed and shaped, and in some cases further crushed, to form samples of terephthalic acid having various bulk densities. The compressing, shaping and crushing operations were carried out employing the same apparatus and conditions as in Example 1.

Each 19.0 kg of terephthalic acid of various bulk densities thus obtained were charged into an esterification autoclave with 12.8 kg of ethylene glycol, 7.6 g of zinc acetate and 11 g of titanium oxide. After replacing the air inside the autoclave by nitrogen gas at a pressure of 2.5 kg/cm^2 gauge, the contents of the autoclave were heated while stirred by a 1 horsepower motor (35 r.p.m.). After about an hour, the temperature was raised to 220°C., and thereafter maintained at that level. The water formed during the reaction was removed from the reaction system through a packed tower, while the inside pressure was maintained at 2.50 kg/cm^2 guage. When the reaction was completed, the transparent, molten product was transferred to a polymerization vessel, and polymerized for 3.3 hours under a pressure of 0.4 mm Hg at 285C., in the presence of 7.6 g of phosphoric acid and 5.7 g of antimony trioxide. For each sample of terephthalic acid, the maximum value indicated in the wattmeter of the motor for driving the stirrer, time required for the esterification, and the colour tone of the product polymer obtained in the above-described operations, is shown in the table below.

Sample No.	bulk density of terephthalic acid	Form of terephthalic acid	Maximum electric power (KWH)	Time required for esterification (min.)	Colour tone b
1	0.52	Powder (average 20μ)	0.84	340	3.6
2	1.35	Tablets (103ϕ × m/m)	0.53	325	1.6
3	1.42	Tablets(10ϕ × 3m/m)	0.52	320	1.8
4	0.93	Crushed tablets (less than 20 mesh)	0.56	320	2.4

As is shown by the above table, when powdery terephthalic acid having a bulk density of 0.52 was used, the 1 horsepower stirring motor was overloaded, but when terephthalic acid having a higher bulk density was used considerably less power was required for stirring. The time required for the esterification was substantially the same in all cases regardless of the density. The colour tone b of the polymer was always lower when terephthalic acids of high density were used, i.e., yellowing of the polymer was less, which of course is generally preferred.

EXAMPLE 3

This is an Example in which a material having a low bulk density was used as a portion of the acid component. The procedure of Example 2 was repeated using 1.9 kg of isophthalic acid having a bulk density of 0.43, 17.1 kg of the sample No. 3 terephthalic acid of Example 2, and 12.8 kg of ethylene glycol. The maximum electric power required at the time of the esterification was 0.55 KWH, and the esterification was completed within 310 minutes. The resultant polymer had a colour tone b of 1.9, and a softening point of 235.4°C.

EXAMPLE 4

The sample No. 1 terephthalic acid and the sample No. 4 terephthalic acid of Example 2 were each used as the material for 15 batch-operations in a plant under the same conditions as in Example 2. The results were as follows:

Terephthalic acid	Average colour tone b of polymer	Presumed average standard deviation	Average softening point
Sample No. 1	3.43	0.59	256°C
Sample No. 4	2.18	0.41	259°C

The above data show that when the acid component of higher density was used, the polymer has a better colour tone and a higher softening point.

EXAMPLE 5

An esterification tank was charged with 13.8 kg of the sample No. 3 terephthalic acid of Example 2, 16.8 kg of 1,4-cyclohexane dimethylol (cis 30%, trans 70%) pre-heated to about 80°C., and 9.4 g of titanium oxide, and within about 60 minutes, the temperature was raised to 238°C. and maintained at this level thereafter. The water formed was distilled off through a distillation tower. Water ceased to distil after 230 minutes from the time at which the inside temperature of the tank reached the aforesaid level. The contents of the tank were then transferred to a polymerization vessel, and polymerized at 295°C. under a reduced pressure, in the presence of 7.0 g of tetrabutyl titanate. The intrinsic viscosity of the resultant polymer was 0.65. The maximum electric power required for stirring the contents of the esterification tank was 0.48 KWH, and the softening point of the polymer was 289.3°C.

WHAT WE CLAIM IS:

1. Process for the production of terephthalic acid, or a mixture of terephthalic acid with at least one different organic dibasic acid, suitable for the formation of polyesters by direct reaction with a glycol, which comprises compressing the acid or mixture of acids and thereafter optionally crushing the compressed mass, the compression, and crushing if used, being such as to give a product having a bulk density of at least 0.8 and an average particle diameter of not more than 8 mm.

2. Process according to claim 1 wherein the compression is such as to give a product having a bulk density of at least 0.9.

3. Process for the production of terephthalic acid according to claim 1 substantially as hereinbefore described.

4. Terephthalic acid, or a mixture of terephthalic acid with at least one different organic dibasic acid, in a form suitable for the formation of polyesters by direct reaction with a glycol, when obtained by a process as claimed in claim 1, 2 or 3.

5. Process for the preparation of polyesters which comprises compressing terephthalic acid, or a mixture of terephthalic acid and at least one different organic dibasic acid, and thereafter optionally crushing the compressed mass, the compression, and crushing if used, being such as to give a product having a bulk density of at least 0.8 and an average particle diameter of not more than 8 mm, reacting the product directly with an alkylene glycol to form a bis-(hydroxyalkyl)-terephthalate or a low molecular weight polymer thereof, and then polymerising the resultant reaction product by heating under reduced pressure.

6. Process according to claim 5 wherein an esterification and/or polymerisation catalyst is present during the reaction of the acid with the glycol.

7. Process for the preparation of polyesters according to claim 5 substantially as hereinbefore described.

8. Terephthalic acid, or a mixture of terephthalic acid with at least one different organic dibasic acid, having a bulk density of at least 0.8, and composed of particles of average particle diameter not more than 8 mm.

9. Polyesters when produced by the process of any of claims 5 to 7.

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